Destructive Analyses Techniques for Safeguards

Mary L. Adamic

June 30, 2009

INL/CON-09-16263

Idaho National Laboratory

Outline

- Destructive Analysis
  - Definitions, Examples, Advantages / Disadvantages
- DA for traditional bulk SNM safeguards
  - U and Pu Assay methods
  - U and Pu Isotopic analysis methods
  - Elemental analysis / trace analysis methods for SNM characterization
- DA for environmental safeguards
  - NWAL program
  - Sample analysis
  - Analytical challenges
  - Quality assurance
- Summary

Destructive Analysis

- Quantitative methods for determining elemental composition, elemental assay, or isotopic composition of a sample
- All or part of the sample is consumed in analysis
  - Sample cannot be recovered (eg. it is volatilized)
- Sample is irreversibly altered
  - Dissolved
  - Radiochemically purified
- Does not necessarily mean important sample attributes are destroyed
  - Analyte separated from matrix, but preserved

Example of DA techniques

- Elemental assay methods
  - Titration
- Elemental composition methods
  - Atomic emission spectroscopy
  - Mass spectrometry
- Isotopic analysis methods
  - Mass spectrometry
  - Alpha spectrometry
  - Radiochemical gamma-ray spectrometry
  - Radiochemical beta or liquid scintillation counting

Destructive Analysis in Safeguards

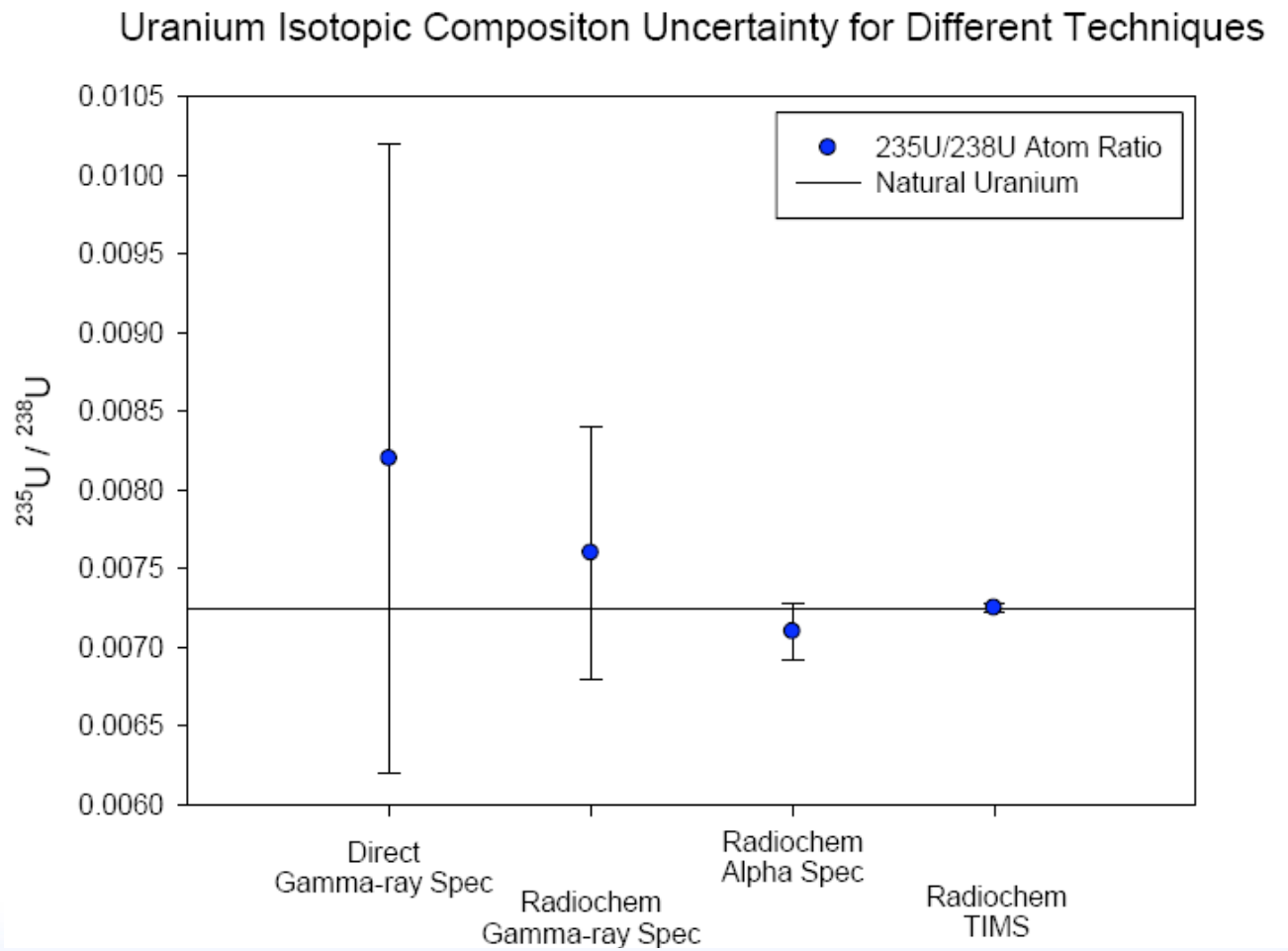
- **Traditional Safeguards**
  - SNM accountability
  - Assay, isotopic, and impurity measurements critical for accurate accounting of SNM

- **Environmental Safeguards**
  - Swipe sampling in safeguarded facilities
  - Isotopic and assay measurements
  - Verification of declared operations
  - Detection of undeclared operations

Advantages of DA techniques

- Precision of DA techniques is usually much better than NDA methods
  - Effect of matrix can be eliminated or corrected
- Detection limits of DA techniques are usually lower than NDA methods
  - Eliminates background from matrix
  - Techniques are generally much more sensitive because of detection method (eg. atom counting vs. activity counting)

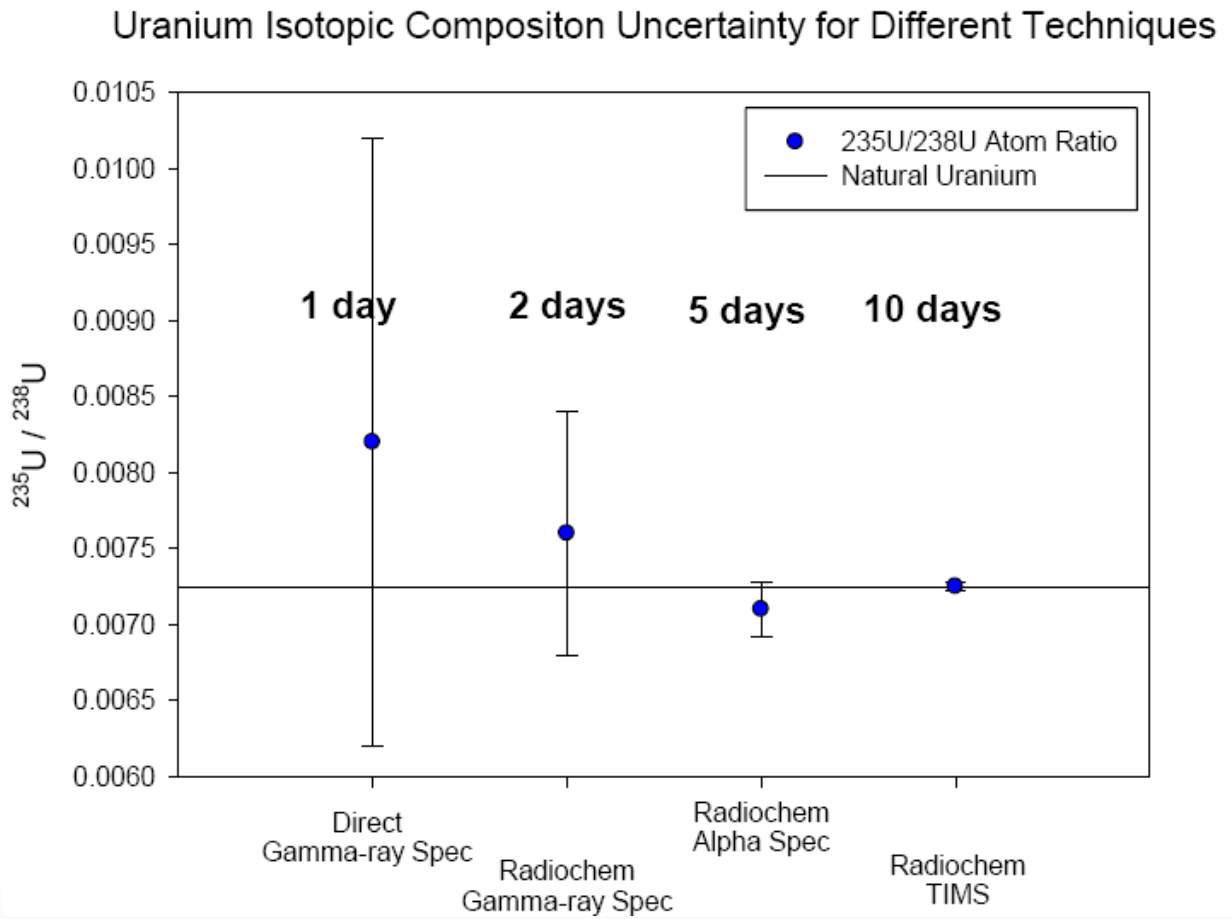
Comparison of precision of NDA and DA Methods



Disadvantages of Destructive Analysis

- Typically much more labor intensive than NDA techniques
  - Sample preparation can take days to complete
- Opportunities to induce problems
  - Cross-contamination of samples
  - Contamination from previous facility operations
- More expensive than many NDA techniques
  - Instruments and supporting facilities are very expensive to build and maintain

Timeline for NDA and DA Methods



Traditional Safeguards DA Measurements

- Uranium and Plutonium Accountability
- Large (mg – g) quantities used to ensure highest measurement precision (~0.5% or better)
- Assay
  - Titration or Isotope Dilution Mass Spectrometry
- Isotopic Analysis
  - Mass spectrometry or (rarely) alpha spectrometry
- Impurity Analysis
  - Atomic emission spectrometry
  - Inductively-coupled plasma mass spectrometry

Davies and Gray Uranium Assay
(Redox or Electrometric Titrimetry)

- Used for a wide range of U materials including metal, oxides, nitrides, and moderately concentrated scrap solutions
- U(VI) is reduced to U(IV) by Fe(II) in H_3PO_4 and then titrated with $K_2Cr_2O_7$ to a potentiometric endpoint

$$U(VI) + Fe(II) \xrightarrow[\text{solution}]{\text{acid}} U(IV) + 2Fe(III)$$

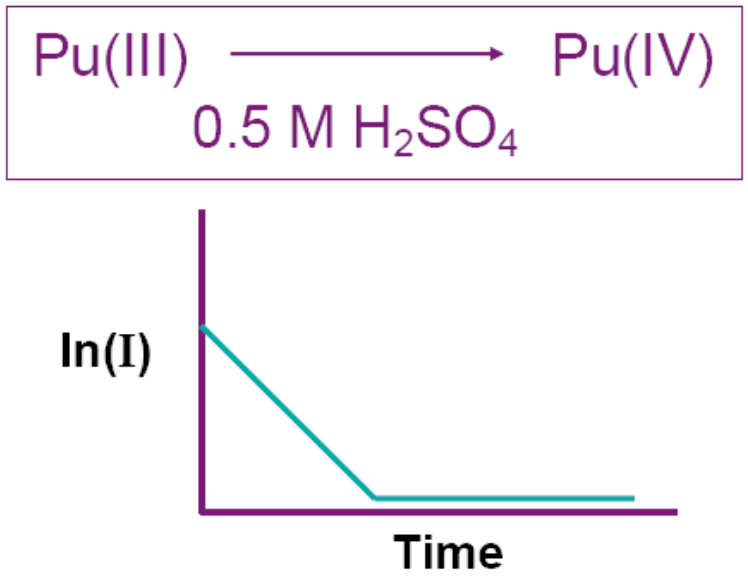
$$U(IV) + Cr(VI) \xrightarrow{\text{catalyst}} U(VI) + Cr(III)$$

Davies and Gray Uranium Assay (cont.)

- Minimal interference by ions typically present in U and U/Pu materials
- Metal samples are typically 300 – 500 mg
- Typically precision is ~0.05%, bias ~0.03 - 0.05%

Coulometric Plutonium Assay Titration

- **Used for a wide range of materials including metals, oxides, salts and solutions.**



Coulometric Plutonium Assay Titration

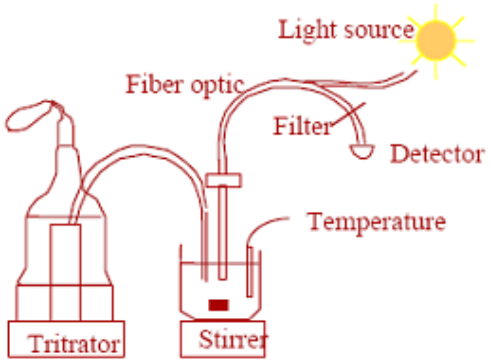
- Interferences include
  - Impurities that oxidize or reduce at 0.670 V (e.g., Fe)
  - Anions that complex Pu(III) or Pu(IV) and shift the potential of the Pu(III)/(IV) couple (e.g., phosphate, phosphite)
  - Components that adsorb onto the Pt working electrode and decrease its electrometric efficiency (e.g., organics, metallic ions —Zr(IV), Hf(IV), Ta(V), and Nb(V)—and elements including Ag, Au, Pd, Pt, Rh, and Ru
- Experienced chemist required
- Amount of Pu determined in an analysis is 5 – 7 mg
- Precision range ~0.08%

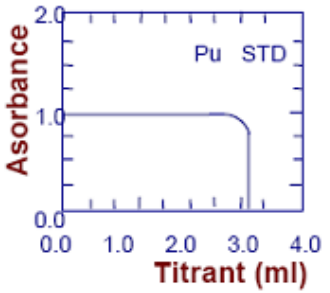
Ceric Titration for Plutonium Assay

- Used for assay of high purity Pu

$$Ce(IV) + Pu(III) \xrightarrow[(HCl/H_2SO_4)]{} Pu(IV)$$

Photometric endpoint is the color change of ferrion



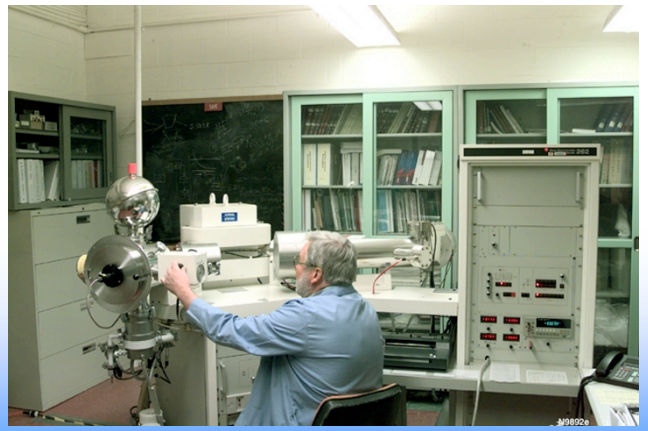


Ceric Titration for Plutonium Assay

- Interferences: U, Np, Fe, and potentially by other metallic elements that have multiple valences
- Alkali metal and alkaline earth metals, Al, Cd, Hf, Zr, Sc and Y do not interfere
- Typically performed using 250 mg sample
- Method can be automated
- Typical precision is 0.05% for an automated method

Assay by Isotope Dilution Mass Spectrometry

- Uranium and Plutonium content can be determined using isotope dilution mass spectrometry (IDMS)
- Known amount of one isotope of an element (preferrably one that is not already present) added to unknown
  - Typically ^{233}U for uranium, ^{242}Pu or ^{244}Pu for plutonium
- Signal strength of each isotope measured relative to the isotope dilution tracer
  - $^{238}U/^{233}U$, $^{236}U/^{233}U$, $^{235}U/^{233}U$, $^{234}U/^{233}U$



Assay by Isotope Dilution Mass Spectrometry (cont.)

- Atoms of each analyte isotope determined from the known amount of tracer added and the measured isotope ratios
  - ^{238}U (atoms) = ^{233}U (atoms) x $^{238}U/^{233}U$
- Convert atoms to grams
  - $$^{238}U\ (g) = \frac{^{238}U\ (atoms)}{6.02e23\ (mol^{-1})} \times 238\ (g \bullet mol^{-1})$$
- Sum isotopes to give total assay
  - Total U (g) = ^{238}U (g) + ^{236}U (g) + ^{235}U (g) + ^{234}U (g)

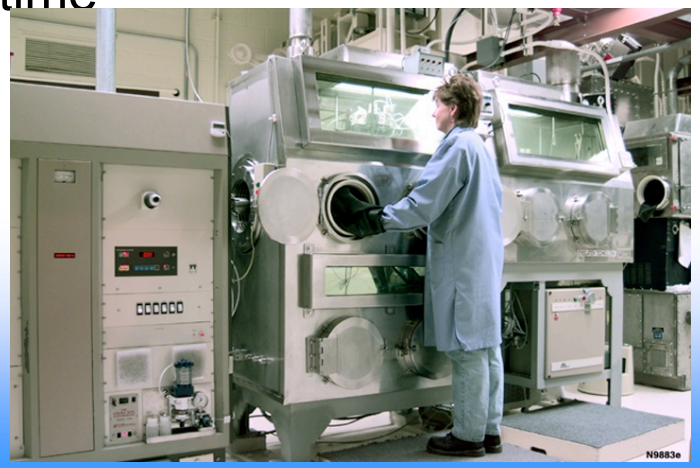
Isotopic Analysis

- Thermal ionization mass spectrometry (TIMS) is benchmark method for determining U or Pu isotopic composition
  - Capable of high precision isotope ratio measurements
  - Abundance sensitivity dependent on instrument design, but 10^{-9} is possible
- Inductively coupled plasma mass spectrometry (ICP-MS) is also viable
  - Magnetic sector instrument preferable

- 0.01 – 1 ng Pu for Pu isotopic analysis by TIMS
- 1 – 100 ng U for U isotopic analysis by TIMS

Trace Metal Analysis

- **Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES)**
  - Primarily use for impurities analysis
  - Provides less precise (~10%) measurement for U, Pu or elemental concentrations
  - Requires sample dissolution
  - Subject to spectral interferences (may require chemical separation)
  - Can analyze many elements at one time
  - Automated instrumentation



Trace impurities by ICP-MS

- Sample must be dissolved
  - Mass interferences
  - Determination of 70 + elements
  - Precision typically 5 – 20 %

Examples of safeguards application

- The time elapsed since a material was last radiochemically purified can be measured using radiochronometry

- Important measurement to verify facility operating history
- Three chronometers measured by TIMS

Age determination using radiochronometers

Sample: PuO_2

Plutonium oxide for MOX Fuel Production

Nuclide	wt %	Nuclide	wt %
^{238}Pu	0.0077	^{234}U	1.475
^{239}Pu	93.7677	^{235}U	73
^{240}Pu	6.1317	^{236}U	17.1
^{241}Pu	0.0737	^{238}U	8.285
^{242}Pu	0.0191		

Ratio	Measured Age* (years)
$^{238}Pu/^{234}U$	0.514
$^{239}Pu/^{235}U$	0.542
$^{240}Pu/^{236}U$	0.528

Average Age: 0.528 years

Typical concentration of ^{241}Pu is 0.14%.
In this sample, ^{241}Pu is 0.0737%.

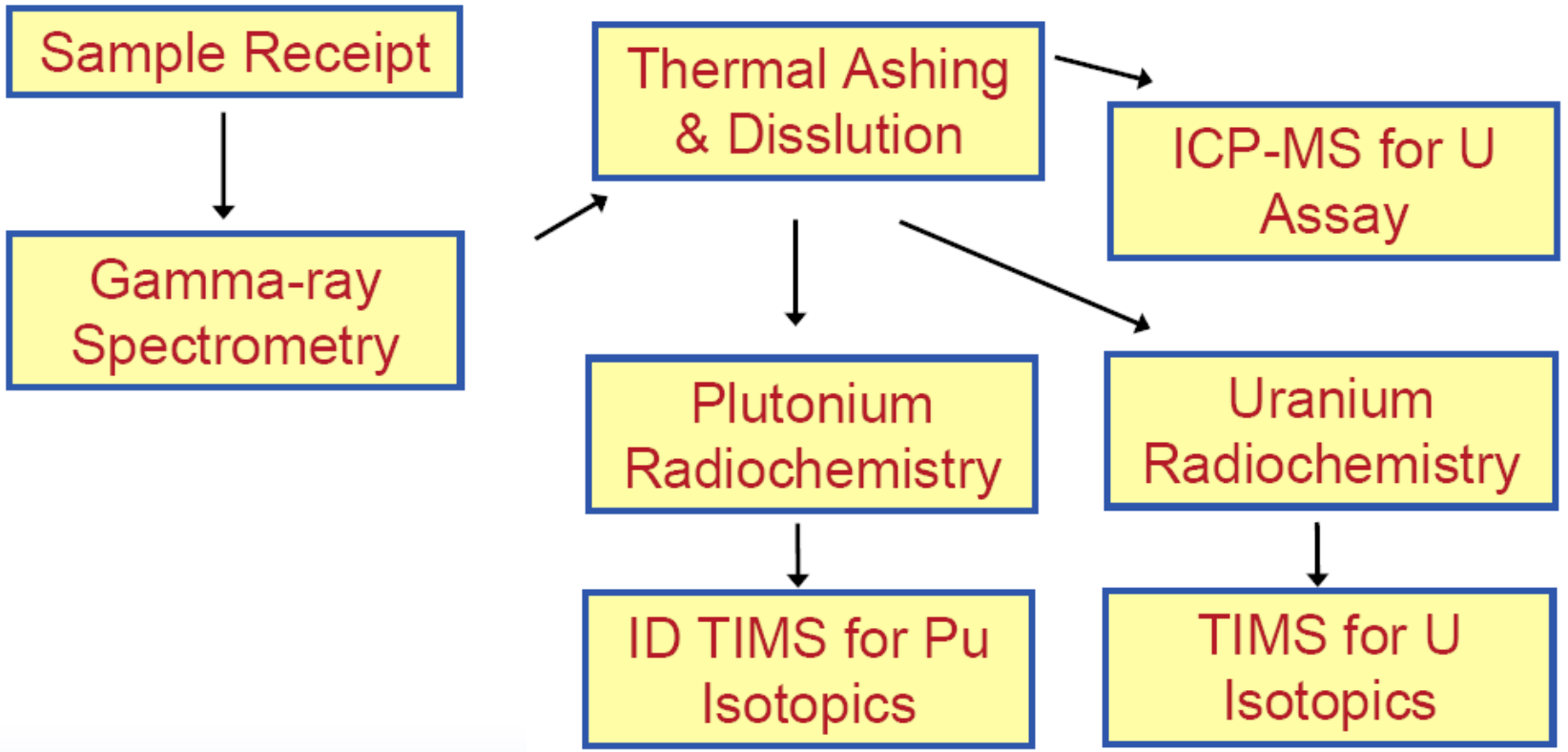
Half-life of ^{241}Pu is 15 years.

DA for IAEA Environmental Safeguards

- Environmental safeguards sampling and analysis is a powerful method for verifying declared operations at safeguarded facilities
- Analyses completed at IAEA Network of World Analytical Laboratories (NWAL)
- Swipe analyses
  - NDA gamma spectroscopy
  - Uranium assay by ICP-MS or ID TIMS, isotopics by TIMS
  - Plutonium assay and isotopics by ID TIMS
- Rigorous QA program
  - Process blanks with each set of samples
  - Blind QC samples analyzed at least once per year
- Much smaller quantities of material than traditional accountability
  - Uranium 1 ng – 10 mg
  - Plutonium 1 fg – 10 ng

LANL photo

NWAL swipe analysis flowsheet



ICP-MS screening

- GOAL: Estimate total U, $^{235}U/^{238}U$, Pu present
- External calibration
- Correction for instrumental drift:
  - Internal standardization ^{115}In
  - External drift monitoring:
    - Identical concentration standards measured at beginning, middle and end of a run.
- Screen for the following radionuclides:

^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu

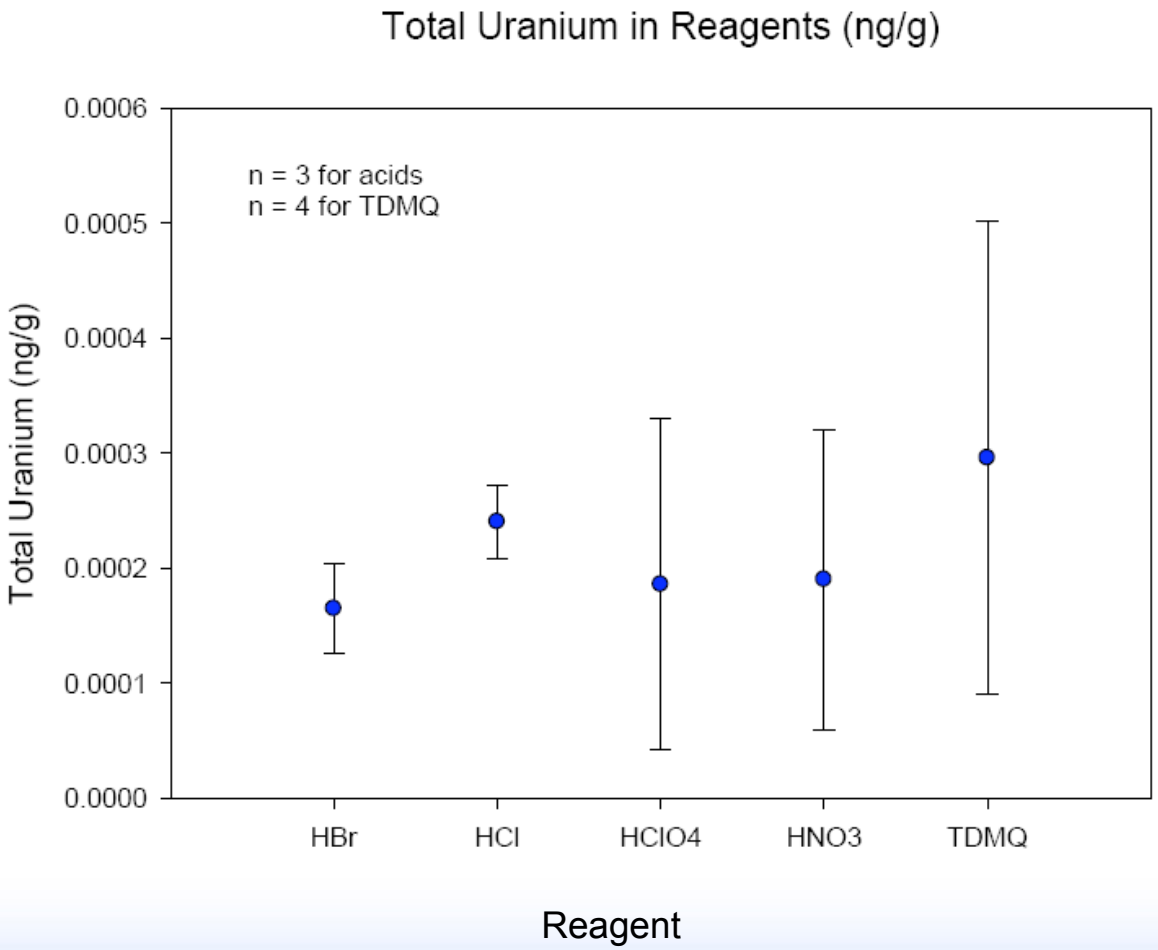
Challenges with Environmental Safeguards DA

- Uranium: 1 ng – 10 mg
  - Huge dynamic range – 7 orders of magnitude!
  - Low end of range is limited by background U in swipes
- Uranium enrichment also challenging
  - Everything from DU up to HEU in samples
- Plutonium: 1 fg – 10 ng
  - Also has a huge dynamic range covering 7 orders of magnitude
  - Low end of range is limited by instrumental detection limits

Uranium Blanks

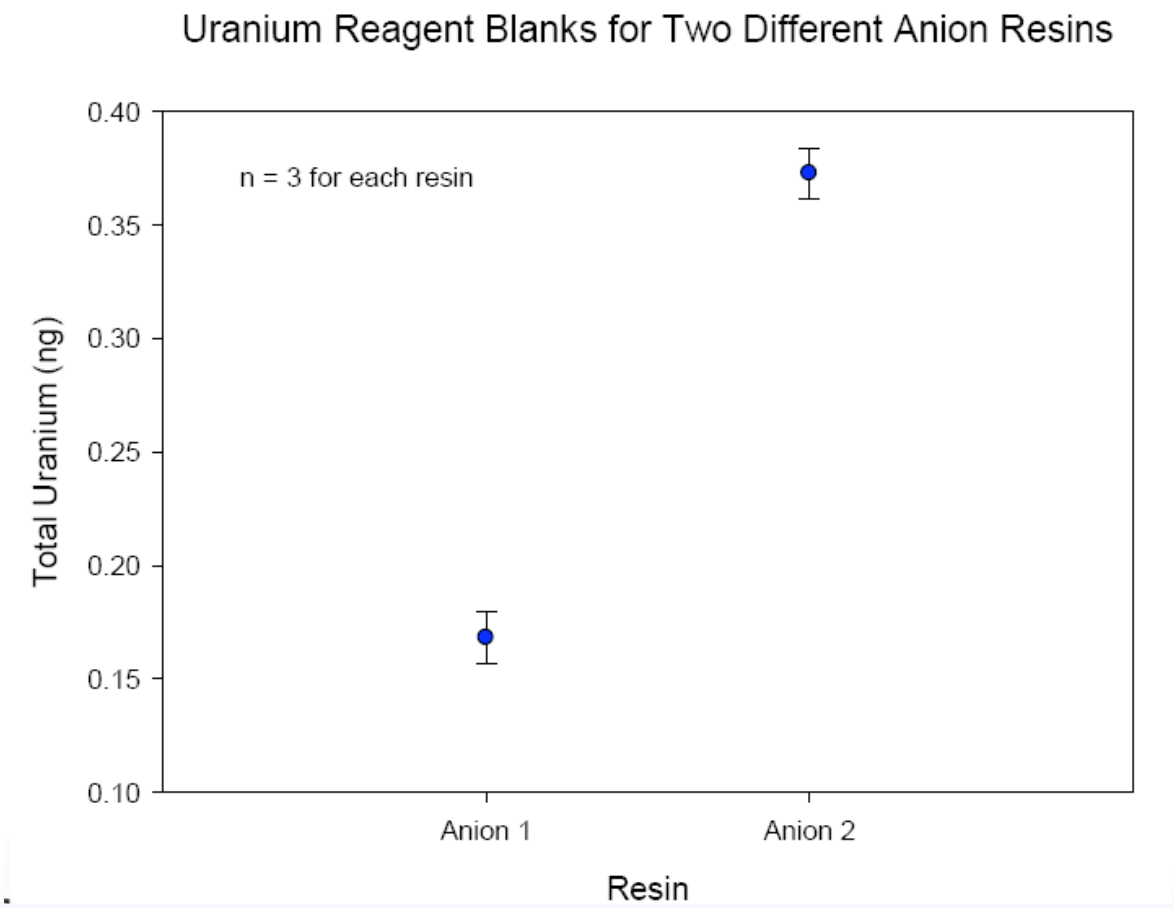
- Thorough understanding of uranium blank contribution needed for precise $^{234}U/^{238}U$ and $^{235}U/^{238}U$ measurement
  - Many samples near natural, low U content
- Careful evaluation of U blank sources
  - Reagents
  - Anion exchange resin
  - Furnace type
  - Radiochemistry laboratory

Typical Uranium concentrations in reagents



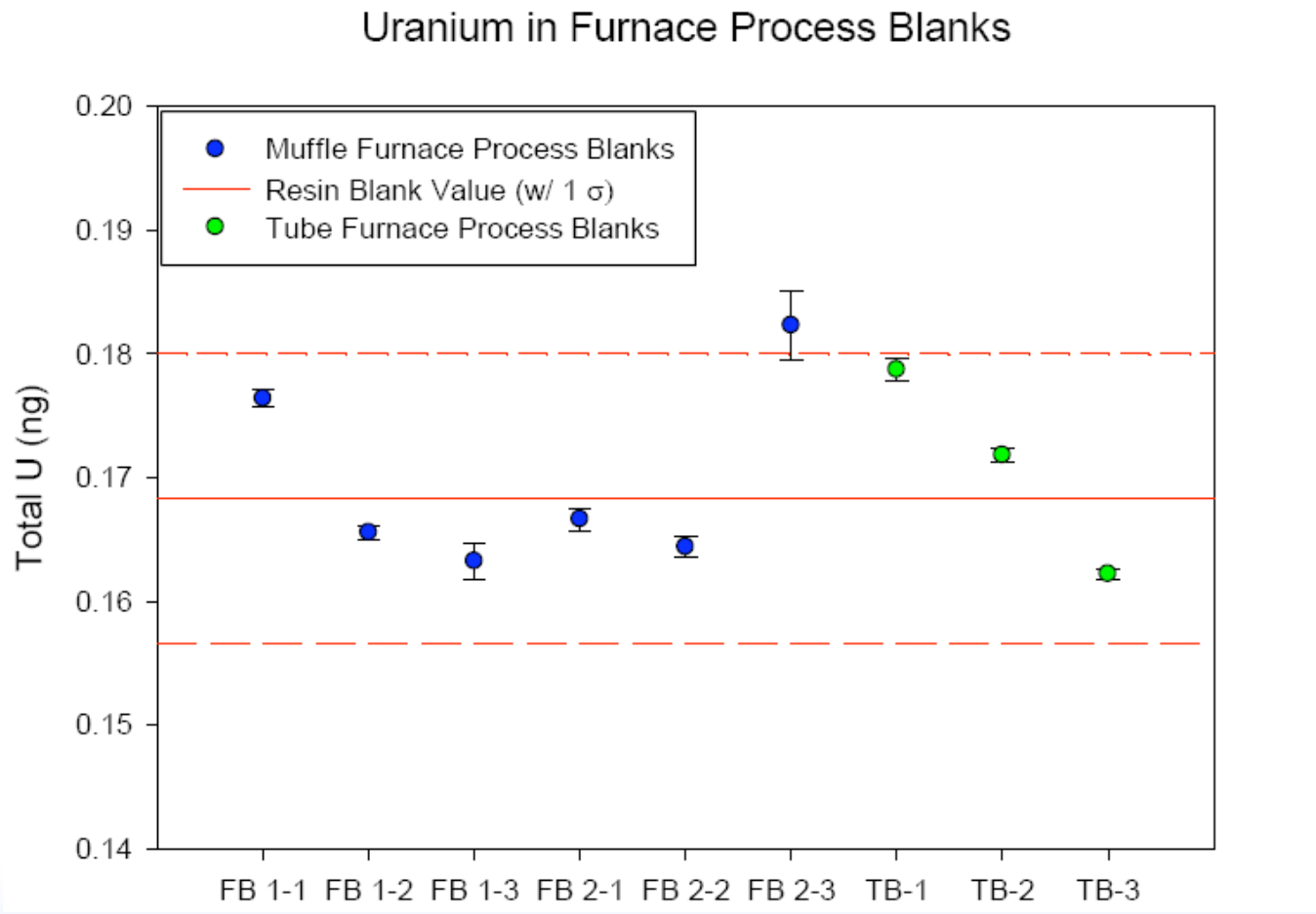
Source: LANL

Uranium in Anion Resins



Source: LANL

Uranium in muffle furnaces



Idaho National Laboratory

Source: LANL

Environmental Safeguards Summary

- Extremely large sample dynamic range
  - Multiple facilities and extreme care taken to prevent facility contamination and sample cross contamination
  - Screening by gamma-spec, gross alpha, and ICP-MS
- Blank must be well understood and routinely monitored for best U isotopic sensitivity

Destructive Analysis Summary

- Destructive analysis methods are the benchmark methods for high-precision SNM assay and isotopic measurements
  - Titration methods for traditional safeguards / accountability
  - TIMS / ICP-MS for isotopic analysis
  - IDMS for environmental safeguards

- Quality Assurance is essential for successful DA program
  - Facility considerations
  - Blank control
  - Blind QC exchanges

Acknowledgements

- Uranium blank data and swipe photo were obtained from a LANL presentation “Destructive Analysis Techniques for Safeguards” by Stephen LaMont, Robert Stiener, Lav Tandon, and Paul Mendoza, June 19, 2008

- Photographs of instruments at INL were taken by Jeff Olsen and Mary Adamic